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Paul C. Tompkins
L. B. Farabee
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INTRODUCTION

The analytical procedures customarily used for the gross analysis of fission products in human urine are not satisfactory with respect to the recovery of some elements. The alkaline earth elements, barium and strontium are particularly unsatisfactory in this respect (1). Since these two elements are among the more important long-lived radioactive isotopes produced by the fission of uranium (2) specific analytical methods for their quantitative analysis in sources such as urine are needed.

Such a method should provide a chemical recovery greater than 90 per cent and be reproducible to around ± 5 per cent or better. When very low activities are being determined, it is desirable to retain at the same time, the La^{140} and Y^{90} daughters of Ba^{140} and Sr^{90} respectively to get the maximum possible counting rate.

The method should have several additional attributes to be most useful for routine analyses. It should be rapid and simple, involving a minimum number of steps. It must also provide for the removal of organic and inorganic solids, potassium in particular. This purification is necessary to eliminate self-absorption of the radiations by the sample and the radioactivity from K^{40} as important variables.

This paper describes a method which meets all of the above requirements except that it is not as rapid and simple in operation as one might wish. The method depends primarily on the coprecipitation of the rare earth and alkaline earth elements with calcium phosphate from an alkaline solution, separation of the phosphoric acid from the cations by an ion exchange column,

and, finally, a separation of barium, strontium and rare earths from calcium and magnesium by a chromate precipitation.

EXPERIMENTAL

Part I - The Alkaline Phosphate Precipitation. - Quantitative recovery of barium, strontium and the rare earths can be achieved by a basic phosphate precipitation from urine. Since these elements do not form complexes with the organic materials present in urine, the precipitation can be carried out directly, thereby avoiding the laborious process of ashing the urine sample. This precipitation serves two major purposes; (1) separation of the above elements from sodium and potassium, and (2) separation of organic materials which are present in a urine sample. In order to achieve further separation, the alkaline earth precipitate is dissolved in hydrochloric acid, diluted to approximately 1500 ml, and a second basic phosphate precipitation is carried out.

Several experiments have demonstrated that barium, strontium and lanthanum are quantitatively carried by the alkaline phosphate precipitate at carrier-free concentrations, but that isotopic yttrium carrier must be added for the complete precipitation of yttrium (3). However carriers are added for each element to minimize losses due to adsorption. Procedure:

1. Add concentrated hydrochloric acid to a 1500-ml urine sample to make the urine 0.2 N in hydrochloric acid and yield a clean solution (Note 1).

2. Heat the sample on a hot plate to a temperature of 85° to 90° C.

3. Add carriers as follows: (1) 20 mg strontium, (2) 4 mg barium, (3) 2 mg lanthanum, and (4) 2 mg yttrium.

4. Add 6 ml of 6 M phosphoric acid in order to provide an excess of phosphate to insure complete precipitation of all calcium and magnesium.

5. Set up an electric motor stirrer to provide vigorous stirring for the subsequent precipitation.

6. Add slowly 6 M sodium hydroxide until a basic phosphate precipitate is visible. Continue the addition until the solution is basic to a pH of 8.0 to 10.0. Universal pH paper can be used to determine the pH value in this case.

7. The precipitate is allowed to settle for 2 hours or longer.

8. The supernatant liquid is decanted by suction to the lowest possible level such that the precipitate is not disturbed. Discard the supernatant solution.

9. Sufficient concentrated hydrochloric acid ($\sim$20-25 ml) is added to dissolve the precipitate. This solution is heated to 90° C.

10. Distilled water (90° C) is added to the beaker to build the volume to approximately 1500 ml.

11. Steps 4 through 8 are repeated in order to reprecipitate the basic phosphates.

12. The remaining slurry is poured into a 250-ml centrifuge cup. The precipitate is centrifuged at 1500 r.p.m. for 5 minutes. The supernatant liquid is decanted by suction and discarded.

13. The precipitate is washed one time with approximately 200 ml of water to which 3 or 4 drops of ammonium hydroxide have been added (Note 2).

14. The precipitate is centrifuged at 1500 r.p.m. for 5 minutes. Wash solution is discarded.

<u>Notes for Part I</u>:

1. A solution 0.2 N in hydrochloric acid and a temperature of 90° C will bring any alkaline earths previously precipitated from the urine sample into solution. This will insure exchange between the carriers and the radioactive isotopes which are being sought.

Some silicious precipitate may remain, but it has been found that no significant fraction of the active elements is associated with it.

2. The precipitate is often peptized by the wash solution, presumably due to the removal of adsorbed counter ions which contributed to the initial aggregation of the precipitate. When this occurs, the suspended solid can be recovered by bringing the wash solution to a boil and centrifuging while hot. The colloidal solid is aggregated by this procedure and is combined with the original alkaline phosphate precipitate.

Part II - Removal of the Phosphate Ion. - The alkaline phosphate precipitate which occupies a volume of ~100 ml, can be dissolved in 10-20 ml of concentrated nitric acid or hydrochloric acid. The resulting solution which occupies a volume of ~50 ml contains approximately 15 mM of cations and about 10 mM of phosphate. Calcium plus magnesium accounts for about 10-12 mM of the total cations. The remainder is due to the carriers which were added, plus an indeterminant quantity of sodium , potassium and ammonium ions and organic material adsorbed on the gelatinous precipitate.

The organic matter is destroyed by wet ashing in the presence of nitric acid and hydrogen peroxide. The phosphate can be removed by adsorbing the cations onto a cation exchange resin (Dowex 50) from a solution about 0.3 to 0.5 molar in cations at a pH of 0.6 ± 0.2. A higher salt concentration leads to a break through of calcium and alkaline earth activities. A pH >1 leads to the rapid precipitation of the rare earth phosphates. When the cations are eluted in the normal manner with 6 M nitric acid, or 6 M hydrochloric acid, the alkaline earth activities are eluted quantitatively in the first 50 ml of eluent. However, around 20 to 30 per cent of the lanthanum is still on the column after the passage of 200 ml of the eluent.

This behavior has been demonstrated to arise from the equilibrium distribution of lanthanum between 6 M nitric acid and the Dowex resin. There

is ~80 per cent of the lanthanum in the solution and around 20 per cent on the resin at equilibrium. This difficulty has been circumvented by inverting the column before the elution begins so that the rare earths need to pass over the minimum quantity of resin during the process of elution.

Procedure:

1. The phosphate precipitate from step I,14 is dissolved in approximately 15 ml fuming nitric acid.

2. The solution is transferred to a 400-ml beaker, and the contents are evaporated to a volume of approximately 10 ml.

3. The remaining organic matter is destroyed by heating the solution to a temperature just below the boiling point, and by adding alternately fuming nitric acid and 30 per cent hydrogen peroxide. (Note 1).

4. The solution is then slowly evaporated to a point where crystallization starts. The walls of the beaker are washed down with distilled water. The solution is heated for 5 minutes to redissolve the solids.

5. The volume is then built to 400 ml with distilled water and the pH of the solution checked with a pH meter. Nitric acid or ammonium hydroxide is added to achieve a pH of 0.60 ± 0.20.

6. The solution is then passed over Dowex 50 cation exchange resin (50 to 80 mesh size) at a flow rate of 1.0 to 1.2 ml/min/cm^2. (Note 2).

7. A 50-ml wash solution of 0.1 N nitric acid is then passed over the column.

8. To elute the cations from the column, the following steps are used:

   (a) Remove the funnel.

   (b) Insert a glass wool plug (see Note 2) and provide a rubber stopper fitted with a one-way stopcock in place of the funnel, being careful that no air bubbles are trapped.

   (c) Invert the column and allow the resin to settle.

(d) Elute the cations with 200 ml 6 N nitric acid at a flow rate of 1 ml/min/cm^2.

9. Evaporate the eluent to a volume of .3 ml or less.

10. Wash the solution into a 150-ml beaker, with distilled water. (The volume should be less than 20 ml at this stage.)

Notes for Part II:

1. Best results are achieved by adding 1/2 to 1 ml fuming nitric acid dropwise from a pipette. Then add dropwise 4 to 6 drops of 30 per cent hydrogen peroxide. This is repeated until a clear solution results.

2. The column is a cylindrical glass tube 18.5 cm long and 1.8 cm inside diameter. The bottom is fitted with a one-way stopcock supported in a one-hole rubber stopper. Glass wool over the rubber stopper holds the resin bed. Fifteen grams of dry resin in the hydrogen form is put into the column. A funnel fitted with a one-hole rubber stopper in the top of the column serves as a reservoir for the influent liquid.

Part III - Removal of Calcium and Magnesium by Strontium Chromate Precipitation. - The solution obtained from Part II contains from 100 to 500 mg calcium, 100-200 mg magnesium, 20 mg strontium, 2 mg barium, 2 mg lanthanum and 2 mg yttrium. The best available method for separating the barium and strontium quantitatively from the calcium and magnesium under conditions which will carry the lanthanum and yttrium with the barium-strontium fraction is that described by Swift (4).

By this procedure, barium chromate is precipitated from a buffered solution at pH 5-6, then strontium chromate is precipitated from the barium chromate supernatant solution at pH 8 in the presence of alcohol. Since both barium and strontium are to be precipitated simultaneously, the conditions described by Swift were reinvestigated.

The experiments were set up according to the factorial design (5) to study the role of the different variables. These experiments have established the following facts:

1. More consistent results were obtained if the temperatures and concentrations of acetate and ammonium hydroxide prescribed by Swift were retained. A complete reexamination of methods for pH control did not seem justified.

2. Satisfactory results were obtained if the potassium chromate concentration of the final solution was between 0.17 M and 0.34 M.

3. The initial volume of solution had to be kept to around 15 ml to give a final volume of around 53 ml. Solubility losses of both strontium and barium exceeded 5 per cent at larger volumes. The rate at which the potassium chromate was added was immaterial.

4. The buffers, potassium chromate and alcohol could be added with no time delays to permit incipient formation of barium chromate before proceeding to the precipitation of the strontium chromate.

5. An alcohol concentration, between 32 and 36 per cent, in the final solution was satisfactory. More dilute alcohol caused loss of both barium and strontium, whereas more concentrated alcohol caused excessive precipitation of calcium chromate.

6. If the solution was stirred mechanically, the alcohol could be added at any rate between 1 and 5 ml/minute. If the stirring was not continuous, a local excess concentration of alcohol developed which led to precipitation of calcium chromate.

7. Calcium chromate was precipitated during the first strontium chromate precipitation, and this led to large and variable losses of both strontium and barium when the precipitate was washed. This was prevented by eliminating the first strontium chromate wash. Instead, the precipitate

was dissolved in 0.2 N nitric acid and precipitated a second time. All transfers of the precipitate from the beakers to the filters was done with a solution equivalent in composition to the strontium chromate filtrate.

8. Even with these precautions, barium was lost to the extent of 2 to 5 per cent in the presence of the quantities of calcium encountered at the initial strontium chromate precipitation step. However lanthanum and yttrium were retained quantitatively in the precipitate. The loss of strontium was not studied specifically, but results on the complete procedure indicate that it could well be between 5 and 10 per cent.

The final procedure takes all of these facts into account, and, if followed carefully, has been found to give satisfactory results.

Procedure:

1. A motor stirrer apparatus is set up such that constant stirring can be had during the subsequent precipitation of strontium chromate.

2. The volume of the eluent is built to 27 ml.

3. While the solution is being constantly stirred, the following solutions are added:

(a) 1 ml 6 M acetic acid

(b) 10 ml 3 M ammonium acetate

(c) 9 ml 1 M potassium chromate

Let stir for 5 minutes

(d) Add ammonium hydroxide dropwise to produce a color change to yellow.

(e) Add 5 ml concentrated ammonium hydroxide.

(f) Add ethyl alcohol (95 per cent) at a flow rate of 3.0 ml/min. ± 1.0 ml/min. to build the alcohol concentration to 35 per cent ± 1.0 per cent.

4. Allow the precipitate to stand for 15 minutes after final addition of the alcohol (Note 1).

5. Filter the precipitate on a medium sintered glass filter (60 ml capacity).

6. Dissolve the precipitate from the filter by using 25 ml 0.2 N nitric acid (Note 2).

7. Transfer again to a 150-ml beaker.

8. Repeat steps 1 through 4.

9. Filter the strontium chromate precipitate on a medium porsity sintered glass filter (Note 3).

10. Wash the precipitate with two wash solutions as follows:

    (a) 20 ml of the filtrate from a strontium chromate precipitation (Note 4).

    (b) 10 ml of 50 per cent ethyl alcohol to which has been added 1 ml of concentrated ammonium hydroxide.

Counting:

The final precipitate is dried in an oven at 100° C before counting. The filter is then placed in a holder equipped with an adjustable screw such that the height of the precipitate can be adjusted to top shelf level in the standard beta-gamma chamber.

Notes on Part III:

1. The 15-minute standing period was recommended by Swift (2) and was not investigated further in this work.

2. It is necessary to dissolve all of the precipitate from the filter in a minimum of nitric acid. It is recommended that a series of aliquots of 5 to 10 ml of the acid be used in the following manner: (1) The aliquot of acid is used to dissolve the residual precipitate clinging to the beaker.

(2) The precipitate is broken loose from the filter with a glass stirring rod and stirred in the acid medium. (3) Suction is applied and the liquid is pulled through the filter. (4) The above procedure is repeated with the remaining aliquots of 0.2 N nitric acid to be used.

3. This filter is a standard sintered glass filter of 30 ml capacity, the top of which has been cut off just above the sintered disc. The edges are ground such that the top can be mounted on the filter and sealed with stopcock grease to provide a leakproof joint. The top can then be detached and the filter can be mounted in such a way that the activity can be counted directly.

4. To provide quantitative transfer of the strontium chromate from the beaker to the filter and to wash the precipitate on the filter, a wash solution is prepared which is saturated with respect to calcium chromate and strontium chromate and which also contains other ions in a concentration equivalent to that found in the filtrate of the strontium chromate precipitation described in the procedure above. The precipitation described in steps 1 through 4 are done from a solution containing 600 mg of calcium. The precipitate is filtered and the filtrate is used for the wash. Aliquots of approximately 5 ml of the wash solution are used. The walls of the beaker and filter can be scrubbed down with a rubber policeman, using the wash solution to finally concentrate the precipitate on the filter.

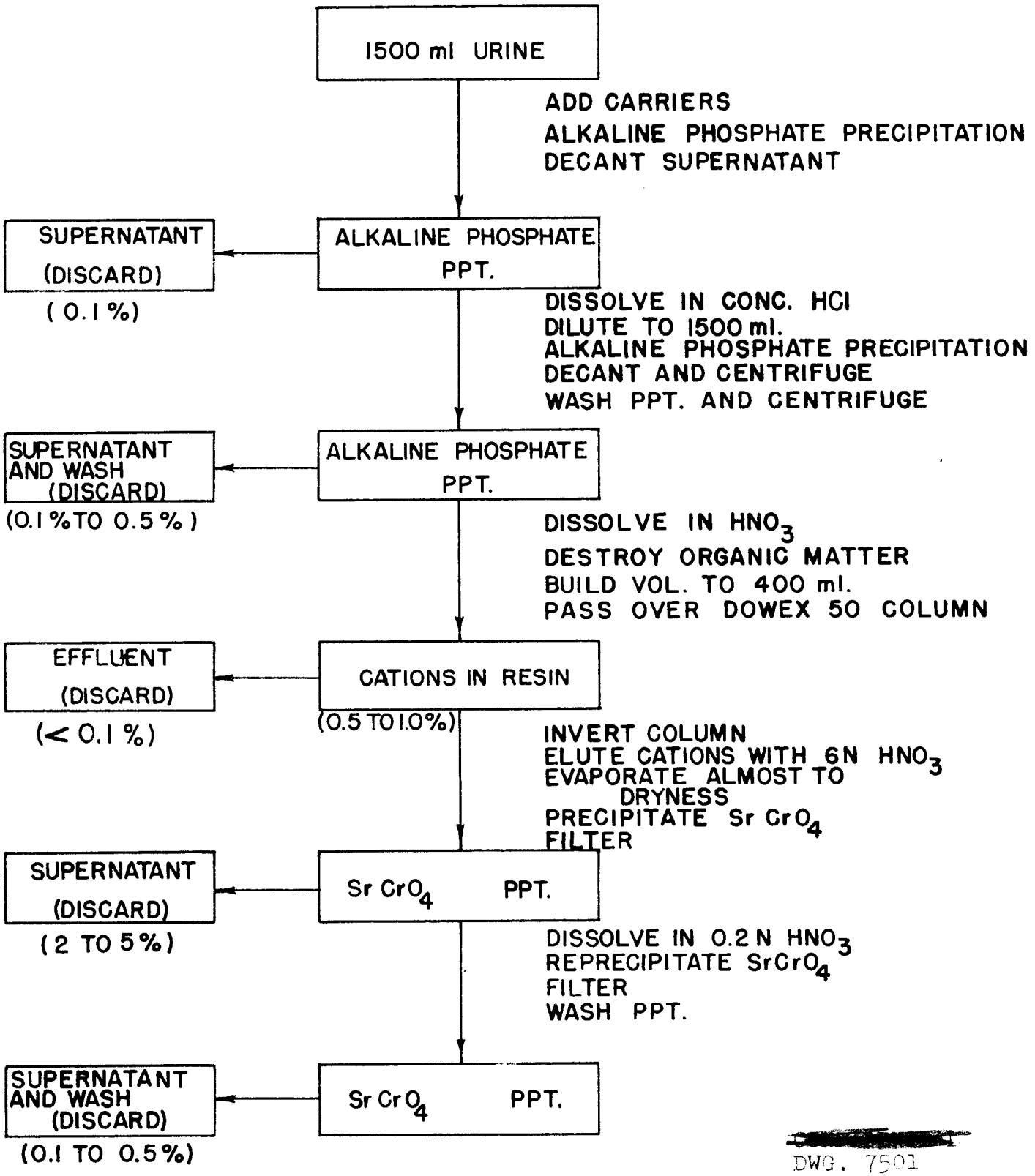
RESULTS

The procedure is outlined as a flow sheet in figure 1. The more detailed studies of the various steps indicated that lanthanum and yttrium should be recovered quantitatively except for slight mechanical losses which are inevitable in a complicated procedure. The approximate losses of barium at each step are indicated below each fraction which is discarded. Only an over-all

FIGURE I

FLOW SHEET

PROCEDURE FOR RADIOCHEMICAL ANALYSIS OF BARIUM, STRONTIUM AND RARE EARTHS IN HUMAN URINE



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recovery was determined for strontium, so the detailed losses at each step are not known at the present time.

Several analyses were made to determine the recovery of each element. A sample of normal urine (1500 ml) was spiked with about 10,000 c/m of carrier-free Ba^{140} - La^{140} in one case and with a similar quantity of Sr^{90} - Y^{90} in the other. The complete analysis was then performed, the final strontium chromate precipitate being dissolved from the filter and quantitatively transferred to a Coors capsule.

For comparison of tracer recovered to tracer added in the experimental runs, the standards were made up as follows:

(a) A quantity of solid carrier equivalent to the final precipitate in the counting capsule of the recovery runs was prepared by a standard strontium chromate precipitation. The precipitate was filtered and dissolved into a Coors capsule. An equal amount of tracer was added to each capsule as was added to the urine sample prior to the alkaline earth phosphate precipitation. (Standards prepared in triplicate).

(b) The standards and the experimental samples were counted under conditions as identical as possible and within one hour from the time of the last precipitation. The samples were counted at intervals until radioactive equilibrium had been achieved. The Ba^{140} - La^{140} samples were counted on Shelf 2 with no added absorber, whereas the Sr^{90} - Y^{90} samples were counted under 100 mg/cm^2 aluminum absorbers so that only the 2.2 Mev beta of Y^{90} was measured.

The results, presented in table I, show that the rare earths were usually recovered quantitatively, the losses occurring in the barium and the strontium. Since the loss of barium was around 3 to 5 per cent whereas the loss of strontium was around 10 per cent, precise corrections for chemical recovery cannot be applied unless the active element being determined is known.

Table I

Recovery of Barium, Strontium, Lanthanum, and Yttrium in the Alkaline Phosphate Procedure for the Analysis of these Elements in Human Urine

Run No.	Barium Recovered (per cent)	Lanthanum Recovered (per cent)
1	100	100
2	95	95
3	102	97
4	101	100
5	95	95

	Strontium Recovered (per cent)	Yttrium Recovered (per cent)
6	91	99
7	93	97
8	86	93
9	87	93

However, the chemical recovery is high enough so that such corrections are unnecessary for many purposes. A routine correction of 5 per cent is recommended for ordinary analytical work.

SUMMARY

A procedure for the simultaneous analysis of radioactive barium, strontium and rare earths in human urine has been developed. The method consists of an alkaline phosphate precipitation from a 24-hour urine sample, separation of the phosphate from the cations by means of an ion exchange resin, and separation of barium and strontium along with their lanthanum and yttrium radioactive daughters from calcium and mangesium by the precipitation of strontium chromate from an alkaline solution.

The procedure is essentially quantitative for lanthanum and yttrium provided no significant mechanical loss of a precipitate occurs. The recovery for barium was found to be around 95 per cent, while that for strontium was around 90 per cent. These losses were found primarily in the filtrate from the strontium chromate precipitate.

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